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PRODUCTION OF CHOLINE CHLORIDE-BASED DEEP EUTECTIC SOLVENT WITH HYDROGEN BOND DONOR D-GLUCOSE AND ETHYLENE GLYCOL

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Abstract

Deep eutectic solvent (DES) is a new environmental friendly solvent. The characteristics of the salt molar ratio greatly influence the characteristics of DES /hydrogen bond donor (HBD) and HBD constituent species. DES was synthesized from salt ChCl and HBD D-Glucose and Ethylene Glycol at different molar ratios will be observed. Freezing, density, pH and viscosity are some characteristics of DES. The result showed that the molar ratio ChCl:D-glucose to generate DES with freezing point and density was the lowest in the molar ratio 2:1 (<20 °C and 1.26352 g/ml) and the molar ratio of ChCl:Ethylene Glycol to generate DES with freezing point, density and viscosity was the lowest on the molar ratio 1: 2.5 (<10 °C, 1.11473 g/ml and 22.049 cP). In addition, the ChCl/D-Glucose-based DES and ChCl/Ethylene Glycol which was produced has a pH in the neutral range

Keywords: Choline Chloride, D-Glucose, DES, Ethylene Glycol, Hydrogen Bond Donor.

Introduction

The problem that the chemical industry has long been facing is dependence on the usage of large volumes of an organic solvent which is hazardous, flammable and un environmental-friendly. As a result, there is significant pressure in the areas of social, economic, and political environment to reduce and replace the use of organic solvents with organic solvents that are more environmental friendly [1]. To overcome these problems, the ILs has been accepted as a new revolutionary chemicals compounds that are more environmental friendly. This new group of chemicals can



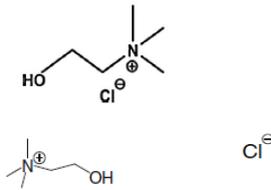
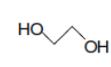
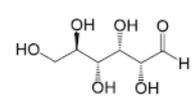
reduce the usage of hazardous organic solvents and the pollution it caused [2]. However, environmental friendliness shown by ILs is still lacking because the ILs does have some limitations, such as: (1) too expensive if imidazolium and pyridinium-based because it costs (5-20) times higher than the cost of conventional organic solvents [3]; (2) have the same toxicity or even higher than the organic solvents [3]; (3) low biodegradation generally [3]; (4) too expensive for larger applications because ILs can not be synthesized well in the laboratory by one-step synthesis [4]; (5) multi-stage purification process is needed to purify the ILs after synthesized have a fairly high production costs [4]; (6) a high degree of purity is required for their impurity although in small amounts will affect the physical properties of ILs [5]; and (7) synthesis ILs very un-environmental friendly [5].

DES has recently emerged as an alternative low cost ionic solvents. Some authors also stated DES as a good like iLs because of DES has physical and solvent properties that are comparable to the ILs, such as density, viscosity, refractive index, conductivity and surface tension [6,7]. However, DES is structurally different from the ILs, which can have the kind of ionic and non-ionic connected by a tissue of hydrogen bonds [8]. In addition, DES has the advantage, that is non-toxic , non-reactive to water and biodegradable, so it has as good as an environmental friendly solvents that are applied to various industrial applications that can replace iLs because of the same characteristics [9,8]. Now, DES has an important role in the field of synthesis of biodiesel, such as a solvent to remove the catalyst from the biodiesel [10], as a solvent to remove glycerol from biodiesel [11], as a reaction medium in enzymatic synthesis of biodiesel [12] and as co- solvent in the synthesis of biodiesel [13].

Typically, a DES is generally compiled by a combination of HBD and halide salt and will produce a liquid at room temperature which has a lower melting point from each of the constituent components [14]. Where, HBD interaction with the quaternary salt will reduce the strength of the electrostatic anion-cation, there by reducing the freezing point of the mixture [15]. One of the most widely used component for the production of DES is ChCl as it is a cheap quaternary ammonium salt, biodegradable and non-toxic in combination with the HBD such as urea, carboxylic acid (eg, oxalic acid), polyols (eg, glycerol) or alcohol (eg, ethylene glycol) [16,17]. Where, the urea, ethylene glycol and glycerol is HBD most widely used for it is cheap and easy to diffuse [18]. Leron, et al., [17] in 2012 reported that the DES of ChCl with urea, ethylene glycol and glycerol as the HBD and as mentioned that in the same molar ratio (ChCl:HBD) freezing point DES of ethylene

glycol is the lowest compared to DES from urea and glycerol. Otherwise, Maugeri, et al., [15] in 2012 reported that the group saccharides (ie, xylitol, D-sorbitol and D-isosorbide) can be derived as HBD in shaping DES and DES produced have a liquid form at room temperature. In the Hayyan research, et al., [19] in 2013 also reported the manufacture of DES based ChCl with saccharides type (D-glucose) as HBD and reported that the physical properties DES produced, such as density, viscosity, surface tension, refractive index and pH almost similar to generally ILs. The production of the DES was mainly influenced by the chemical properties of the constituent components, such as the type and molar ratio of ammonium salt and HBD, temperature and moisture content [19,5].

Table 1. Structure of Salt and HBD Use to Synthesis the DES [18]

Salt	HBD	
ChCl	Ethylene Glycol	D-Glucose
		
Cation	Anion	

DES was synthesized from salt ChCl and HBD D-Glucose and Ethylene Glycol will be studied. In Table 1 is shown the structure of salt and HBD constituent. DES based on the influence of the molar ratio, that is des characteristics including freezing, density, pH and viscosity will be observed ChCl: HBD (D-Glucose and Ethylene Glycol) and which type of HBD (D-Glucose and Ethylene Glycol) at temperature ($30\text{ }^{\circ}\text{C} \pm 2\text{ }^{\circ}\text{C}$) and then look for the best condition of variable process in the range observed.

Materials and Methods

In this work, choline chloride ($\text{C}_5\text{H}_{14}\text{ClNO}$) as salt and D-Glucose ($\text{C}_6\text{H}_{12}\text{O}_6$) and Ethylene glycol ($\text{C}_2\text{H}_6\text{O}_2$) as hydrogen bond donors were obtained from Sigma-Aldrich. The synthesis DES is made by fixed variables such as stirring speed (400 rpm), time (2 hours), temperature ($80\text{ }^{\circ}\text{C}$) and the type of salt (ChCl) as well as the independent variables such as the type of HBD (D-Glucose and

Ethylene glycol) and the molar ratio of salt: HBD, namely ChCl:D-glucose (1:1; 1.25:1; 1.5:1; 1.75:1; 2:1; 2.25:1 and 2.5:1) and the molar ratio of ChCl: ethylene glycol (1:1; 1:1.25; 1:1.5; 1:1.75; 1:2; 1:2.25 and 1:2.5).DES is obtained by heating the salt ChCl and HBD D-glucose / ethylene glycol at certain molar ratio simultaneously up to temperature of 80 °C while stirring using a magnetic stirrer for 2 hours and after the heating process, colourless liquid called DES is obtained [19].

The freezing point of DESs was measured by looking the form of DES at temperatures 30 °C (± 2 °C), 20 °C(± 2 °C) and 10 °C(± 2 °C). DES in turbid white liquid at 30 °C (± 2 °C) showed that the freezing point of DES is above 30 °C (± 2 °C). While DES in colourless liquid at 30 °C (± 2 °C) showed that the freezing point of DES is below 30 °C (± 2 °C). However, to minimize the range of freezing point DES, DES form was analyzed at temperatures 20 °C (± 2 °C) and 10 °C (± 2 °C). If DES in colourless liquid at 20 °C (± 2 °C) showed that the freezing point of DES is below 20 °C (± 2 °C) and if DES in colourless liquid at 10 °C (± 2 °C) showed that the freezing point of DES is below 10 °C (± 2 °C). The pH of DESs was measured by using a pH meter and the density was measured by picnometric method and the viscosity was measured by Ostwald's viscometer at 30 °C (± 2 °C).

Results and Discussion

Effects of Salt and HBD Molar Ratio on DES Characteristics

From the result, after the heating process was completed, DES 1 to 14 were in colourless liquid, then DES obtained was let to be cool until it reaches the room temperature (30 °C ± 2 °C). At room temperature all DES were still in a colourless liquid although some DES turn out to be more viscous and turbid white liquid, which is DES 7 and 8, as shown in Table 2 and Table 3. DES in colourless liquid at room temperature showed that the freezing point of DES is below room temperature (30 °C ± 2 °C) because there was not any form changing. While turbid white liquid DES indicates that the freezing point of DES is above room temperature (30 °C ± 2 °C) because at room temperature form DES become more viscous and white.

Furthermore, to minimize the range of freezing point DES, DES form was analyzed at temperatures 20 °C (± 2 °C) and 10 °C (± 2 °C), as shown in Table 2 and Table 3. From Table 2 shown that at a temperature of 20 °C (± 2 °C) DES 1 to 3 are at turbid white liquid form, DES 4 to 5 in the

colourless liquid form and DES 6 to 7 in the turbid liquids form. However, at a temperature of 10 °C (± 2 °C) DES are all in turbid white liquid form.

Table 2. The Codes and Forms of ChCl/ D-Glucose-Based DES

Molar Ratio		Form		
ChCl: D-Glucose	Code	30 °C	20 °C	10 °C
		(± 2 °C)	(± 2 °C)	(± 2 °C)
1 : 1	DES 1	Colourless liquid	Turbid white liquid	Turbid white liquid
1,25 : 1	DES 2	Colourless liquid	Turbid white liquid	Turbid white liquid
1,5 : 1	DES 3	Colourless liquid	Turbid white liquid	Turbid white liquid
1,75 : 1	DES 4	Colourless liquid	Colourless liquid	Turbid white liquid
2 : 1	DES 5	Colourless liquid	Colourless liquid	Turbid white liquid
2,25 : 1	DES 6	Colourless liquid	Turbid white liquid	Turbid white liquid
2,5 : 1	DES 7	Turbid white liquid	Turbid white liquid	Turbid white liquid

Table 3. The Codes and Forms of ChCl/ Ethylene Glycol-Based DES.

Molar Ratio		Form		
ChCl: Ethylene Glycol	Code	30 °C	20 °C	10 °C
		(± 2 °C)	(± 2 °C)	(± 2 °C)
1 : 1	DES 8	Turbid white liquid	Turbid white liquid	Turbid white liquid
1 : 1,25	DES 9	Colourless liquid	Colourless liquid	Colourless liquid
1 : 1,5	DES 10	Colourless liquid	Colourless liquid	Colourless liquid
1 : 1,75	DES 11	Colourless liquid	Colourless liquid	Colourless liquid
1 : 2	DES 12	Colourless liquid	Colourless liquid	Colourless liquid
1 : 2,25	DES 13	Colourless liquid	Colourless liquid	Colourless liquid
1 : 2,5	DES 14	Colourless liquid	Colourless liquid	Colourless liquid

So the best molar ratio to produce a DES D-Glucose-based is the molar ratio of ChCl and D-Glucose 1.75: 1 and 2: 1. This is because at those molar ratio DES with the lowest freezing point ($<20^{\circ}\text{C}$) is obtained. This is parallel with the research which is done by Hayyan, et al., [19] in 2013, that the D-glucose-based DES at a molar ratio of ChCl: D-glucose = 2:1 is obtained lowest freezing point, which is 15°C . It compared with the freezing point of ChCl which ranges from $302-305^{\circ}\text{C}$ and freezing point D-Glucose that is equal to 146.1°C , freezing point D-Glucose-based DES is smaller than the freezing point of its constituent. From table 3 it can be seen that the DES 9 to 14 are in colourless liquid form at temperature 10°C ($\pm 2^{\circ}\text{C}$). It can be concluded that except the molar ratio of ChCl and molar ratio of Ethylene Glycol 1: 1, DES Ethylene Glycol-based has a low freezing point ($<10^{\circ}\text{C}$).

According to research Zhang, et al., [5], in 2012 DES in colourless liquid form is formed by mixing salt and HBD at certain molar ratios. At the molar ratio of HBD has a strong ability to form hydrogen bonding interactions with ChCl. A colourless liquid or this new phase of DES showed decrease in the value of the freezing point and is generally characterized by a lower freezing point than the two constituent solids [20,5]. The low freezing point of DES caused by hydrogen bonds and a complex interaction of HBD and halide salt anion thus reducing the grid energy in the mixture leads to a decrease in the value of freezing [21,20].

As for the DES in turbid white liquid, the possible reason is the molar ratio of HBD and salt is not right. DES 7 with a molar ratio of ChCl: D-Glucose = 2.5: 1 obtained DES in turbid white liquid form at a temperature of 30°C while in DES 6 to 1 with the same number of D-Glucose and the decreases the amount of salt ChCl obtained DES with a colourless liquid form. It is caused by high concentrations of ChCl compared to HBD D-Glucose, so there is a halide anion ChCl excess salt in the mixture. In addition, D-Glucose also does not have HBD more to build a hydrogen bond with the ChCl halide anions excess. Therefore, the mixture became turbid white liquid and freezing point DES is not decreasing but increasing.

However, in Table 2 showed that at temperature 20°C ($\pm 2^{\circ}\text{C}$) DES 1 to 3 are in turbid white liquid, DES 4 to 5 are in colourless liquid and DES 6 to 7 are in turbid white liquid. The form changing of DES 1 to 3 became turbid white liquid at temperature 20°C ($\pm 2^{\circ}\text{C}$) is probably caused by the presence of hydroxyl group (-OH) of the excess HBD D-Glucose in the mixture too, so when the temperature decrease the hydroxyl group (-OH) of the excess HBD D-Glucose causes DES in

turbid white liquid. while when ChCl increase DES 4 to 5 are still in the colourless liquid, it is caused by the availability of halide anions of salt ChCl to build a hydrogen bond with the hydroxyl group (-OH) of HBD D-Glucose. However, if the halide anion of salt ChCl is also excessive, it will cause DES in turbid white liquid, such as DES 6 and DES 7.

Similarly with DES 8 with a molar ratio ChCl: Ethylene Glycol=1:1 is obtained DES inturbid white liquid, while DES 9 to 14 with the same number of ChCl and the amount of HBD Ethylene Glycol increase is obtained DES incolourless liquid. In the case of DES 8, concentration of ChCl is higher than the HBD Ethylene Glycol or otherwise concentration of Ethylene Glycol is low compared with ChCl, so there are excess anion halide of salt ChCl on mixture and Ethylene Glycol does not has HBD again to build hydrogen bonds with the excess anions halide. Therefore, the mixture in the turbid white liquid and DES has freezing point is higher than the other DES.

In addition, the results of research the influence of the molar ratio of ChCl: D-Glucose against freezing point has been done, it was found that the research is parallel with the research that was done by Hayyan, et al., [19] in 2013 about the making ChCl-based DES and groups of saccharides (D-glucose) as HBD, that at room temperature DES in molar ratio ChCl: D-Glucose = 1:1; 1.5:1 and 2: 1 obtained DES in colourless liquid and DES in molar ratio ChCl: D-Glucose = 2.5: 1 at room temperature becomes more viscous and turbid white liquid. As well as the effect of the molar ratio ChCl: Ethylene Glycol against freezing point, it was found that the research is parallel with the research that has done by Bagh, et al., [4] and research that is done by Shahbaz, et al., [22], that the molar ratio ChCl: Ethylene Glycol = 0.36: 0.64; 0.33: 0.67 and 0.28: 0.72 obtained DES in the colourless liquid at room temperature and the freezing point DES were lower than room temperature.

From the research D-Glucose-based DES and Ethylene Glycol have freezing point below room temperature. When compared with another DES which is made from different salt or HBD and has been widely studied, such as ChCl-based DES and urea which has freezing point 12 °C at molar ratio of ChCl: urea = 1: 2, ChCl-based DES and glycerol has freezing point -40 °C at molar ratio of ChCl: glycerol = 1: 2 and ChCl-based DES and malonic acid has freezing point 10 °C at molar ratio of ChCl: malonic acid = 1: 1 [5]. It can be concluded that DES which consists of D-Glucose and Ethylene Glycol are DES that has potential as a cheap and safe solvent in various fields because those DES have a lower freezing point of 50 °C like the other DES [19].

The density is needed to understand the behaviour of a liquid substance [8]. In general, one of the important physical properties of ionic liquids is density and specifically in DES [23]. Data about DES density has an important role in the application of environmental friendly solvent [22]. DES density is usually determined gravimetrically and the molar ratio of salt/HBD has a significant effect on the density of the DES resulted [14,8]. In Figure 1 and Figure 2, the chart shows the influence of the molar ratio of ChCl: D-glucose and the molar ratio of ChCl: Ethylene Glycol vs DES density values.

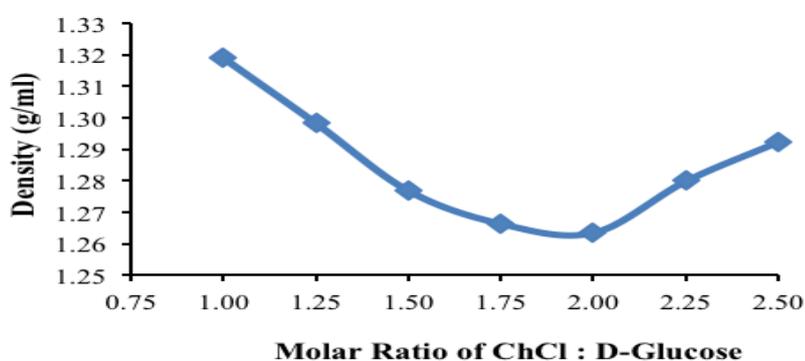


Fig.1. Effects of Molar Ratio ChCl: D-Glucose on Density of DES.

From the graph of the influence of the molar ratio of ChCl: D-Glucose in Figure1, it's indicated that all density of DES values were above 1.25 g/ml. These values are situated between ChCl density and density of D-glucose at room temperature, respectively 1.1856 gr/ml and 1.5345 gr/ml. Therefore, research conducted in line with Shahbaz's research, et al., [23] in 2011, that the density of DES is situated between the density of salt and HBD constituent.

From the graph, it's also indicated that the density values decreased from DES 1 of 1.31895 g/ml to DES 5 of 1.26352 g/ml but increased in DES 6 and DES 7, respectively amounted to 1.27988 g/ml and 1.29234 g/ml. In the previous section mentioned that the value of ChCl salt concentration higher than the concentration of HBD, it is caused halide anions in salt exceed so that the freezing point of DES increased. it can be seen that what is written by figure 1, it can be seen that the density of DES 6 and DES 7 is increased. The presence of excess halide anions in the mixture caused the mixture in turbid white liquid and it also led to the greater mass of the mixture so that the density of

the mixture obtained is also getting bigger. Therefore, it can be concluded that the presence of halide anions extra salt in the mixture will lead to increased density of DES.

The result showed that the lowest density was at DES 5 with molar ratio ChCl: D-Glucose = 2:1. The results are consistent with Harris' research [24] and Hayyan, et al., research [19], that the ChCl/D-glucose-based DES reaches the eutectic point at molar ratio of ChCl: D-glucose = 2:1 because in these molar ratio obtained lowest density, as well as the lowest freezing point value was also obtained at these molar ratio.

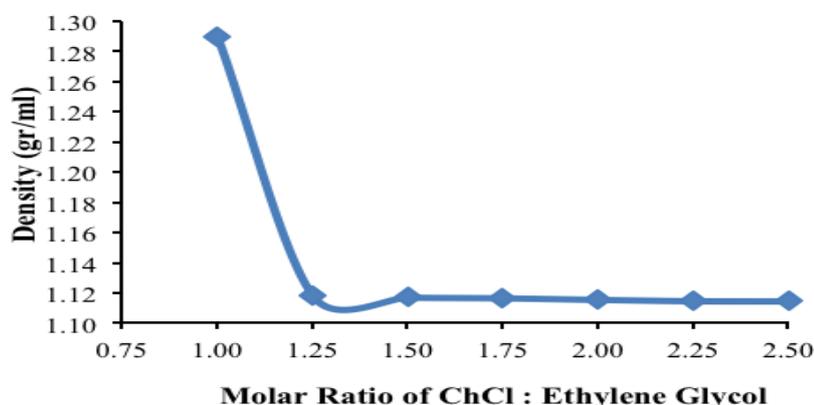


Fig. 2. Effects of Molar Ratio ChCl: Ethylene Glycol on Densities of DES.

From Fig.2. shows that all DES density were above 1.11 g/ml. This value is between density of ChCl and density of Ethylene Glycol at room temperature, each is 1.1856 gr/ml and 1.11 g/ml. Therefore, research was conducted in line with the Tang, et al., research [14] in 2015, that the DES density value is higher than the density of water and also higher than the density of the constituent HBD.

From the graph in Figure 2 is also shown that the density decreased from DES 8 to 14. The highest density value is DES 8 of 1.28974 g/ml at molar ratio of ChCl: Ethylene Glycol = 1: 1 and the density DES declines as the increasing number of Ethylene Glycol. The lowest density of DES is DES 14 amounted to 1.11473 g/ml, which the molar ratio of ChCl: Ethylene Glycol = 1: 2.5.

In Table 3 it can be seen that the DES 8 in turbid white liquid at room temperature. So in the density, DES 8 also has the highest density of other DES. This is caused by the presence of excess halide anions of salt ChCl in the mixture and HBD of Ethylene Glycol is no longer available to

build hydrogen bonds. So that the mass density of the mixture increases and DES is too. While the amount of ethylene glycol increased, density is decreased, it is caused by HBD of Ethylene Glycol available to bond with the hydrogen halide anions from ChCl. Moreover, this can be explained by the value of Ethylene Glycol density is smaller than the density of ChCl, so by the number of Ethylene Glycol increased the DES density value will be decreased [25].

The result showed that the D-Glucose-based DES has density above 1.25 g/ml and ethylene glycol-based DES has density of approximately 1.11 g/ml. If compared with other DES originated from different salt or HBD, such as tetrabutylammonium bromide (TBABr)-based DES as salt and ethylene glycol, 1,3-propanediol, 1,5-pentanediol and glycerol as HBD, where in the HBD concentration of 66.7 % (w/w) DES density values obtained were below 1.1 g/ml at 30 °C [8]. ChCl-based DES as salt and glycerol as HBD, where ChCl concentration of 33% (w/w) DES density values obtained 1.18 g/ml at 20 °C [24]. N,N diethylen ethanol ammonium chloride-based DES as salt and glycerol as HBD, DES density obtained is above 1.15 g/ml at 30 °C while using ethylene glycol as HBD DES density is ± 1.1 gr/ml at 30 °C [22]. It can be concluded that ChCl-based DES and D-glucose has density value tends to be higher than other DES and ChCl-based DES and ethylene glycol has density value tends to be lower than other DES.

The final conclusion is the molar ratio of ChCl: D-Glucose and ChCl: Ethylene Glycol greatly affect the value of the density of DES. This is according to research conducted by Shahbaz, et al., [22] in 2012 and the research conducted by Tang, et al., [14] in 2015, that the consists of the constituent DES has a significant effect on the density of DES.

pH is one of the most important characteristics of a liquid as it can help the selection of the type of pipe to be used for construction materials and corrosion-related aspects of the design. pH also has an influence in a reaction mainly in bioreaction [19]. The chemical properties of the components of DES mainly HBD greatly affect the strength of the acid or base DES, so it can produce DES with pH alkaline, neutral or acid [5,26]. The Figure 3 and 4 show the influence of the molar ratio to ChCl: D-Glucose and ChCl:Ethylene Glycol on pH of DES at room temperature.

From Fig. 3 the influence of the molar ratio of ChCl: D-Glucose against pH, it can be seen that the pH obtained DES increased from DES 1 to 5, which is 6.70; 6.76; 6.80; 6.88 and 7.05 but the pH decreased in DES 6 and 7, respectively 6.96 and 6.91. In the discussion of freezing point and

density, the presence of excess halide anions salt ChCl increase the freezing point and the density of DES. As well as the pH, the DES 6 and DES 7 shown increase in pH.

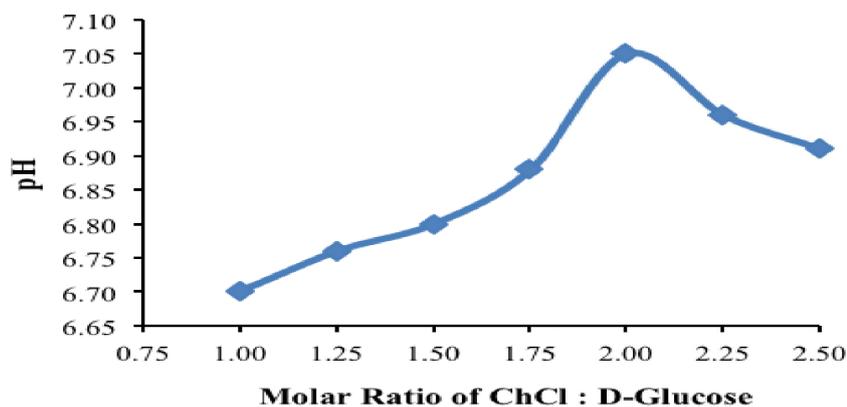


Fig. 3. Effects of Molar Ratio ChCl: D-Glucose on pH of DES.

It is also caused by the higher concentration of ChCl compared to the concentration of D-glucose, so excess anion halide salt ChCl in the DES does not bind to the HBD D-Glucose, this make the pH of DES will decrease to pH of free ChCl in the mixture, ChCl has pH ranging from 5 to 6.5. In general, the pH of D-glucose-based DES obtained from the research is about pH 7 or neutral, it is supported by the research of Hayyan, et al., [19], Zhang, et al., [5] and Maugeri, et al., [15], that the DES with sugar HBD has a neutral pH at room temperature. Therefore, the sugar-based DES suggested to be applied in the fields of chemical, environmental and biological [19,15].

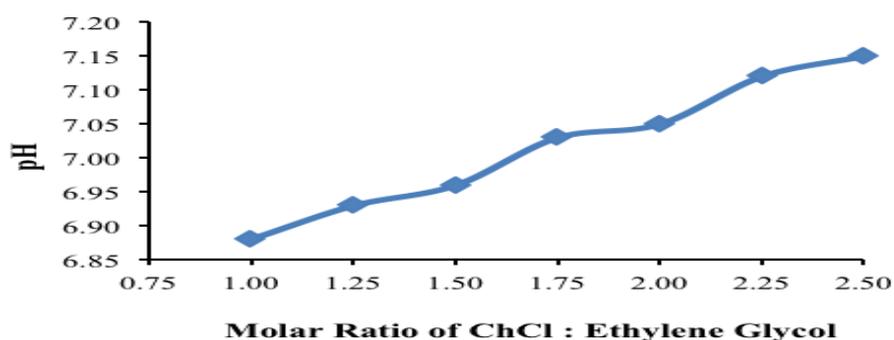


Fig. 4. Effects of Molar Ratio ChCl: Ethylene Glycol on pH of DES.

Figure 4 shows that the pH of DES increased with the increase of HBD Ethylene Glycol, i.e from molar ratio of 1:1 to 1:2.5. pH of DES is 6.88; 6.93; 6.96; 7.03; 7.05; 7.12 and 7.15. the pH of obtained DES is around pH 7 or pH neutral.

In research by Zhao, et al., [27] in 2015 on the ChCl-based DES that is applied as a solvent in the extraction of Rutin (flavonoids) of *Sophora japonica*. In the study of biocompatibility of DES as a biocompatible and biodegradable solvent using bacteria, it is found that DES with HBD-based amine, alcohol and sugar of bacterial growth will not be inhibited, such as DES with pH in the range of pH neutral and otherwise DES with organic acid-based HBD inhibit bacterial growth caused by the changes of pH. pH of tested DES for bacterial growth must be well below the optimal pH (6.5-7.5). Thus, research studies conducted support Zhao, et al., [27] that the DES with an alcohol-based HBD (ethylene glycol) and sugar (glucose) has a pH in the range pH neutral. So the research conducted agreed with the research Protsenko, et al., [28], Naser, et al., [25] and Zhao, et al., [27], that the nature of the salt and HBD constituent DES affect the acidity or alkalinity of DES. Viscosity is an important property that needs to be known because the application of DES is highly dependent on the viscosity value [20,29]. Knowing the value of the viscosity of the DES can facilitate the creation of DES with optimum molar ratio suitable for a particular application. It also can save the energy in the manufacturing process DES [19]. DES development with low viscosity is desirable because of the potential to partially DES friendly media environment [20]. The lower viscosity of DES, the better it is used as a solvent [29]. Viscosity is influenced by the interaction of hydrogen bonding, van der Waals and electrostatic. Based on the interaction between molecules, the viscosity of DES is certainly higher than some other conventional solvents, but similar to the viscosity of the ionic liquid [27]. The viscosity of the eutectic mixture of DES mainly influenced by the chemical nature of the constituent components, salt and HBD [20].

In this study, the viscosity of 7 D-glucose-based DES can not be measured caused by it is highly viscous at room temperature. This led to D-Glucose-based DES is less potential as a solvent and as a environmental friendly media. According to research Hayyan, et al., [20] and Kow, et al., [29] the lower viscosity of the DES is the better it is used as solvent and as a environmental friendly media. In addition, the DES which is in colourless liquid at room temperature would make it easier to handle so it can be used in various types of industries [19].

High viscosity DES due to the presence of excess hydrogen bonding interactions that cause stronger van der Waals and electrostatic interactions between the two components of the excess resulting in lower mobility in the molecule in the DES. This will affect the composition of the eutectic mixture of DES, DES generated such characteristics will be different [20,29]. According to Zhao, et al., [27] in 2015, the large amount of hydroxyl groups on HBD will cause excess hydrogen bonds thereby increasing the attractive forces between the molecules and make the fluid more viscous. According to Yusof, et al., [8] in 2014, the salt acts as a bridge connecting the ionic groups in the DES. The amount of salt that can cause less tissue between the groups in the DES became scarce, causing a decrease in viscosity. While in this study, the amount of salt ChCl increase so the bond become stronger between the DES and DES obtained become more viscous (high viscosity).

Due to the high viscosity value, the D-Glucose-based DES is advised to be preheated before it is applied [19]. However, according to Kow, et al., [29] in 2015, raising its temperature to reduce the viscosity of DES will lead to increasing time, power and cost of the process. So according to research by Zhao, et al., [27] in 2015, another alternative that is expected to reduce the viscosity of the sugar-based DES to be easy to apply by adding water. The addition of water to the ChCl/D-glucose-based DES in molar ratio ChCl: D-Glucose: Water = 2.5: 1: 2.5 produces DES with viscosity 584 cP at 30 °C, this value is much lower than the value of the viscosity of ChCl/D-Glucose-based DES that is in the range 8,000-12,000 cP at 25 °C [42,19]. In the study Maugeri, et al., [15] in 2012 also discuss how to reduce the viscosity D-Glucose-based DES. Maugeri, et al., [15] add glycerol at a molar ratio of ChCl: D-Glucose: glycerol = 1: 0.5: 0.5 and DES viscosity values obtained at 4,430 cP at 30 °C. While DES without the addition of glycerol in a molar ratio ChCl: D-Glucose = 1:1 DES viscosity value can't be measured.

The molar ratio of ChCl: Ethylene Glycol = 1:1 DES is so viscous and turbid, so viscosity value can't be measured. But viscosity 6 Ethylene Glycol-based DES others can be measured. From Figure 5 shows that DES is the Ethylene Glycol- based DES with a relatively low viscosity, wherein the viscosity DES obtained is below 100 cP at room temperature. The research agreed with the research by Zhang, et al., [5] in 2012 that unless the ChCl/Ethylene Glycol-based DES, most DES has a relatively high viscosity (> 100 cP) at room temperature. From Figure 5 is also shown that the viscosity obtained DES decreased along with increasing the number of HBD Ethylene Glycol, ie

from a molar ratio of 1: 1.25 to 1: 2.5, the viscosity of DES is respectively 33.001; 29.561; 28.534; 26.447; 22.849 and 22.049 cP.

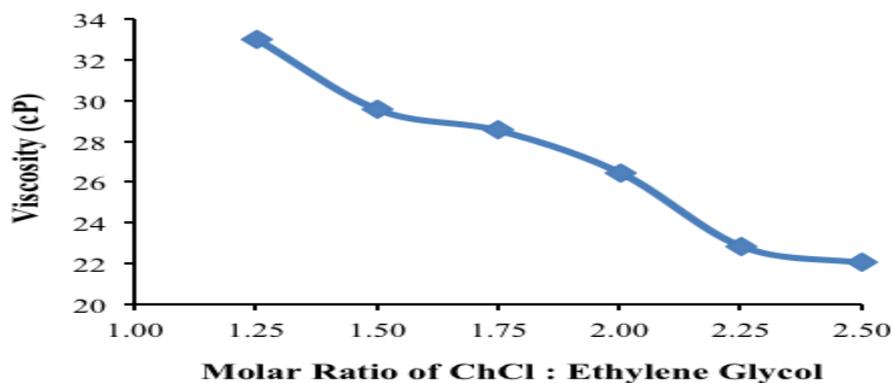


Fig. 5. Effects of Molar Ratio ChCl: Ethylene Glycol on Viscosities of DES

So the research conducted agreed with the research conducted by Yusof, et al., [8] in 2014, that the viscosity decreases with increasing of HBD Ethylene Glycol. According to Yusof, et al., [8] the molar ratio of salt and HBD where the amount of salt remain same while the amount of HBD increase, the salt may act as a bridge connecting the other ionic groups. The amount of salt that can cause less bond between the groups in the DES became scarce, causing a decrease in viscosity.

When compared with other DES originating from different salt or HBD, such as DES from ChCl based and urea, glycerol and malonic acid as the HBD at the same molar ratio, ie 1:2 DES viscosity values obtained respectively 750; 259 and 1,124 cP at 25 °C [5]. It can be produced that D-glucose-based DES has a viscosity value tends to be higher than the DES other, while the Ethylene Glycol-based DES has a lower viscosity than other DES, and from the research results are also obtained viscosity values Ethylene Glycol-based DES is relatively low compared to the viscosity of D-glucose-based DES. This is consistent with the theory that the viscosity of DES mainly influenced by the chemical properties of the components of DES, which is a type of ammonium salts and HBD and the molar ratio of salt/HBD [5,8].

Effects of Hydrogen Bond Donor (HBD) Type on DES Characteristics

In this Research, HBD influence on the characteristics of the type of DES are reviewed based on the number of hydroxyl groups (OH) is available for building bonds with the hydrogen halide anion of the salt in a same molar ratio ChCl and HBD. HBD used is D-Glucose and at a molar ratio of 1: 1 is Ethylene Glycol.

Table 4. Forms and Freezing Point of DESs

DES	Form at Room Temperature (30 °C)	Freezing Point
ChCl : D-Glucose = 1:1	Colourless liquid	< 30 °C
ChCl : Ethylene glycol = 1:1	Turbid white liquid	> 30 °C

From Table 4 it can be seen that the molar ratio of 1: 1, D-Glucose-based DES has a lower freezing point than Ethylene Glycol-based DES. This is caused by the amount of hydroxyl group (OH) on D-Glucose more than in Ethylene Glycol. So that at the same molar ratio, hydroxyl group of D-glucose to build more hydrogen bonds with halide anions from the salt ChCl. While in Ethylene Glycol-based DES are halide anions ChCl excess salt causing turbid white liquid DES and has a high freezing point, ie > 30°C. However, if the number of hydroxyl (OH) of HBD overproduction of the DES, it can also lead to increased freezing DES. As in the study Harris, et al., [30] in 2008, ChCl/Erythritol-based DES has a freezing point lower than ChCl/xylitol-based DES, ChCl/D-Fructose and ChCl/D-glucose at a molar ratio of 1:1. Where Erythritol has four hydroxyl (OH), while Xylitol, D-fructose and D-glucose have five hydroxyl group (OH). Therefore, to assess the effect of the freezing point type HBD DES, it is necessary to review the amount of the hydroxyl group (OH) on HBD available to bond with the hydrogen halide anion of the salt ChCl because the hydroxyl group (OH) HBD under or over in the DES can affect the freezing point.

From the graph in Figure 6 can be seen that the density of the D-Glucose-based DES is higher than the Ethylene Glycol-based DES. DES density D-Glucose-based DES is above 1.25 g/ml while the density Ethylene Glycol-based DES be around 1.11 g/ml. This is caused by the number of hydroxyl (OH) D-Glucose in HBD is more than the HBD Ethylene Glycol, where there are 5 hydroxyl group (OH) on D-Glucose and 2 hydroxyl group (OH) in Ethylene Glycol [30]. In addition, it can also be explained by the density Ethylene Glycol smaller than the density D-Glucose, then the addition of

which of HBD D-Glucose and Ethylene Glycol at a same molar ratio will obtain lower density than the density of the D-Glucose-based DES [33].

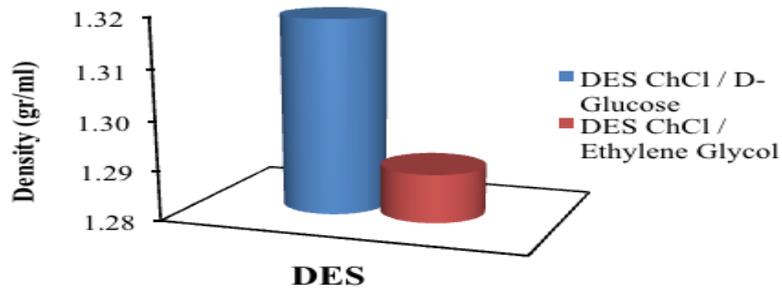


Fig. 6. Effects of HBD on Densities of DES

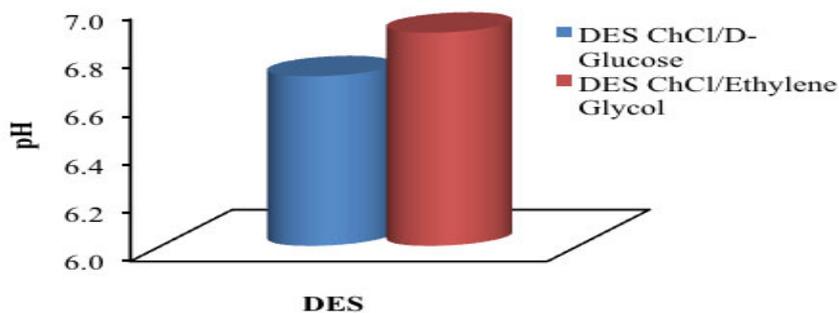


Fig. 7. Effects of HBD on pH of DES

From the graph in Figure 7 can be seen that the pH of Ethylene Glycol-based DES and D-Glucose-based DES in the range of neutral pH, which is respectively 6.88 and 6.70. It is caused by nature of salt ChCl, HBD D-Glucose and Ethylene Glycol which is at the neutral pH range, where ChCl has a pH ranging from 5 to 6.5, D-Glucose has a pH ranging from 5.9 and Ethylene Glycol has the pH ranges from 5.5-7.5. Thus, research conducted agreed with the research by Zhao, et al., [42] that the DES with an alcohol-based HBD (ethylene glycol) and sugar (glucose) has a pH in the range pH neutral.

In this study, the viscosity of D-Glucose-based DES and Ethylene Glycol-based DES at molar ratio of 1:1 can't be measured. This is because the D-glucose-based DES at molar ratio of 1:1 is highly viscous at room temperature and Ethylene Glycol-based DES is viscous fluid and turbid.

On D-Glucose-based DES, the large number of hydroxyl (OH) is available for building bonds with the hydrogen halide anion of salt-based DES ChCl cause D-Glucose-based DES has high viscosity. This is caused by the connection between groups in the DES is getting stronger so that DES obtained more viscous (high viscosity) [8].

Ethylene Glycol-based DES is turbid white liquid. This is caused by the number of hydroxyl (OH) in Ethylene Glycol is not enough to build a hydrogen bond with halide anions from the salt ChCl, so there is a halide anion of ChCl excess salt in the form of liquid DES causes turbid. Therefore, if the number of Ethylene Glycol improved it will obtain colourless liquid DES at room temperature and the viscosity of the DES will decrease.

Conclusions

The molar ratio of ChCl: D-Glucose and ChCl: Ethylene Glycol is a factor that affects the characteristics of the DES can be described below:

- The molar ratio of ChCl: D-Glucose that can produce DES with the lowest freezing point and the density is 2:1, if the number of ChCl is raised or relegated then the freezing point and density of DES will increase.
- The molar ratio of ChCl: Ethylene Glycol to generate DES with freezing point, density and viscosity is the lowest in the molar ratio of 1:2.5, if the number of Ethylene Glycol HBD decreases then the freezing point, density and viscosity of DES will increase.
- ChCl/D-Glucose and ChCl/Ethylene Glycol based DES has a pH in the range pH neutral and Ethylene Glycol-based DES has a relatively low viscosity (<100 cP) at room temperature (30 °C), while the D-Glucose-based DES has a high viscosity.

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